

(19)



Europäisches Patentamt  
European Patent Office  
Office européen des brevets

(11) Publication number:

**0 382 005  
A2**

(12)

## EUROPEAN PATENT APPLICATION

(21) Application number: 90101440.7

(51) Int. Cl.<sup>5</sup>: **C08J 7/04, C09D 139/06,  
G02B 1/10**

(22) Date of filing: 25.01.90

(30) Priority: 30.01.89 AR 313108

(43) Date of publication of application:  
16.08.90 Bulletin 90/33

(84) Designated Contracting States:  
**BE CH DE ES FR GB IT LI NL**

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(54) **Method to prepare pigmented laquers for the coloring of contact lenses, the pigmented or colorless laquers thus obtained and the contact lenses colored with said laquers.**

(57) Object of the invention is a method for preparing pigmented laquers for the forming of color effect in contact lenses, said method comprising forming a prepolymerized gelled mass from UV-photopolymerizable monomers, separating from said gelled mass the residual monomers in order to form a storable mass. The pigmented laquers or varnishes are obtained by dispersing the selected comminuted or micronized pigments in a vehicle formed by said gelled mass or fractions thereof, dissolved in the precursor monomers of same.

**EP 0 382 005 A2**

## Method for coloring contact lenses and lenses made by the same

The present invention refers to a method for the manufacture of inks or pigmented lacquers for the coloring of contact lenses, to the pigmented or colorless lacquers thus obtained and to the contact lenses colored with said lacquers.

This invention is very especially related to the preparation of inks or lacquers for contact lenses formed by polymeric substrates, which make up the lens itself and a layer of color or colored varnish, which is in turn integrated to a partially prepolymerized matrix formulated with monomers, the polymerization of which is completed "in situ". In this manner, the color layer and the substratum remain firmly consolidated or bound through covalent linkage. The fundamental advantages of this invention are the color durability, the lacquer versatility (it may be applied to flexible, hydrophilic and gas permeable lenses) regardless of their constituent chemical groups) and the simplicity of the preparation and application methods.

### Background

It is a well known fact that colored contact lenses, also called "cosmetic" lenses, are mainly designed to enhance or modify the color of the eyes, by applying a layer of color that covers the iris.

The preliminary art includes several endeavors developed with the purpose of producing cosmetic contact lenses, including also ophthalmic prosthesis, of everlasting color. US Patent N° 3.679.504 for instance, proposes the manufacture of soft contact lenses, of many-layers or "sandwich" structure, being the color layer formed or deposited between two transparent layers of hydrophilic polymers (for instance, copolymers of ethyleneglycol monomethacrylate with less than 2% of ethyleneglycol dimethacrylate, (eventually in mixture with the diester) bound by means of an adhesive layer consisting in a mixture of polymerized monomers (of a composition equal or similar to that of said layers) deposited or interposed between the mentioned hydrogel layers. In turn, the color layer is formed before the material or adhesive precursor mixture of monomers is deposited, starting from dyes or pigments applied, for instance, over one of the hydrogel formed layers. In this manner, the color layer is not in direct contact with the ocular fluids and tissues. Apart from the process being rudimentary, these lenses are far too thick.

U.S. Patent N° 3.535.386 also proposed the manufacture of cosmetic contact lenses of multi-layer structure, in which covering of the color layer with a polymerizable liquid material is resorted to. As indicated in US Patent N° 4.668.240, this type of multi-layer lenses are inconveniently thick and furthermore, subjected to the layers' defoliation or delamination, leaving the color layer exposed.

According to the above mentioned US Patents, the materials that make up the contact lenses are hydrophilic polymers, with little reticulation and derived from the polymerization of vinylic monomers (especially acrylic and/or methacrylic esters). Different variations have been also proposed in this aspect, based on the application of other polymerized materials, such as polyurethane, mentioned in US Patents N° 3.786.034, 3.821.136 and 4.359.558.

U.S. Patent N° 4.668.240 (vide supra), describes and claims a method to produce durable colored contact lenses of great flexibility (as far as it refers to the possibilities of obtaining various colors) transparent or opaque, hydrophilic or flexible, and of thicknesses similar to those of the conventional contact lenses. The method covered by this U.S. Patent comprises partially covering a polymeric contact lens with colored material, including the color components carried in a polymeric medium, and then binding both polymeric matrixes, through covalent links produced between compatible and reactable groups, necessarily present in both polymers, and given the case, also in the color components, with the condition that at least one of said reactive groups, is an oxirane or isocyanate group. Said reactable groups are the -COOH, OH and -NH<sub>2</sub> or -NH-alkyl groups. As examples of monomers including said groups, mention is made of various acrylic monomers, methacrylic acid and its esters of hydroxymethyl or hydroxyethyl, aminoalkyl, glyceryl, and besides monomers copolymerizable with the above mentioned, such as N-vinyl-2 pyrrolidone, vinyl esters (vinyl ethyl ether) alkyl esters (methyl acrylate of methacrylate, etc.). As it follows from the above stated, the latter patent has its operative limitations and complications, derived from the essential interaction among the reactive groups, which demands complex formulations and costly checking during the industrial process.

The present invention provides, on the contrary, new reaction mechanisms, of greater versatility than those of all the previous ones and a simple and economical practical industrial application.

## Detailed description of the invention

Lets us now see how it is possible to prepare lacquers or varnishes for the coloring of contact lenses, by means of the method detailed in this invention, based on the processing of specifically formulated polymerizable materials, and according to a determined operative sequence, that results in the formation of pigmented lacquers, which during the curing stage are chemically bound to the prepolymerized material (precursor of the hydrophilic or polymethacrylic substratum that makes up the contact lens properly), thus structuring firmly adhered and wear resistant pigmented layers.

In what is hereinafter claimed, mention will be indistinctly made to colored or colorless inks, lacquers or varnishes, in the individualization, description or preparation of the products obtained through the method which is the object of this invention.

Therefore, the main object of the present invention is a method to manufacture pigmented lacquers or inks for cosmetic lenses, consisting in:

a) to prepolymerize under UV radiation, half of a mixture of:

- 60 to 70% of N-vinyl-2-pyrrolidone (NVP)
- 8 to 12% of 2-hydroxyethyl methacrylate (HEMA)
- 0.3 to 1% of reticulant components
- 8 to 15% of glycidyl acrylate or methacrylate
- up to 13% of cyclohexyl methacrylate or acrylate
- up to 1% of acrylic or methacrylic acid
- 0.1 to 0.5% UV photoinitiator of polymerization

considering these quantities in ponderal parts, under stirring and at ambient temperature, during a sufficient period of time to form a gel having the consistency known in the art.

b) to extract the volatile monomers from said gel, until an easily malleable paste is formed.

c) to let the paste formed in stage b) to settle at ambient temperature, during a period of time enough to have the remainder of monomers it might still contain, separated by exudation.

d) to dissolve the paste with part of the monomers mixture without prepolymerization indicated under point a), in ponderal relation sufficient enough to form a solution at a temperature not higher than ambient temperature, then proceed to filter and recover a transparent, colorless and curable lacquer.

e) to pigment the lacquer of stage d), mixing it with the necessary quantity of the chosen micronized pigment.

With the above described and hereinafter claimed method, pigmented or colorless lacquers or varnishes, storable during periods of up to 6 months (at low temperatures, for instance  $-10^{\circ}$  /  $-20^{\circ}$  C) with no unfavorable changes and consequently, ready to be used, are obtained.

As already pointed out, the lacquers are curable by catalysis, for which reason the preliminary incorporation of appropriate polymerization catalyzers is required prior to its application. For instance, Lupersol 256 (trade mark of a Penwalt Corp. product) or USP 245 (a registered product of Witco Corp.) in ponderal relation of 0.2 to 1% with respect to the mass of pigmented lacquer.

The pigmented or colorless inks or lacquers obtained with the method herein described, may be applied over any prepolymerized surface, cellulosic substratum, etc. This means that the formulation of the substratum to be covered with the ink of the present innovation has no critical importance. It is considered that in this particular aspect of the lacquers as here described, a very important part is played by the reactivity of the glycidyl component whose oxirane (or epoxy) groups react with hydroxyl amino groups of the polymeric substratum, remaining the colored or colorless layer fixed by means of covalent links of well known chemical stability.

The reticulant components have different alternatives; the preferred ones are diallyl maleate, ethyleneglycol dimethacrylate, trimethyl propane dimethacrylate and tri or tetraethylene dimethacrylate and mixtures thereof.

Among the possible polymerization catalyzers, benzoin, diisopropylxanthogendisulfite (Diproxid R of INC Pharmaceutical), and Darocur R (Merck), etc., may be mentioned among others.

The operations from a) to e) may be immediately carried out successively or by steps. It is possible, for instance, to prepare a relatively large mass of the material to be prepolymerized (monomers mixture: HEMA and N-vinyl-2-pyrrolidone, reticulant and the glycidyl component), which is stable when stored at  $18/20^{\circ}$  C, to be used later on (in only one batch or in several fractions), the catalytic component being subsequently incorporated and proceeding then to the mass irradiation (under magnetic or mechanic stirring) with UV (an appropriate UV source are the actinic tubes Phillips ILA 20W 05).

This prepolymerization operation is carried out at ambient temperature between  $15$  and  $20^{\circ}$  C and it continues until the mass gets a consistency or viscosity that indicates an appropriate polymerization

degree. A lapse of time of 60 to 90 minutes is generally sufficient to reach such polymerization degree, shown by an evident thickening of the mass, that acquires consistency and oily dripping. At this point the polymerization progress is stopped by turning off the UV and cooling the container in a bath of  $-30^{\circ}$  to  $-40^{\circ}$  C (refrigerated acetone or alcohol bath), while stirring is continued. The resulting mass has a gel consistency, storable at low temperatures ( $-18^{\circ}$  /  $-25^{\circ}$  C), or ready to be immediately processed.

Stage b) above corresponds to the formation of a paste with the prepolymer formulated in stage a). If the gel has been kept in conservative storage at  $-18^{\circ}$  /  $-25^{\circ}$  C, it is left to acquire ambient temperature and then treated by any means known in the art, for all the time necessary to extract the free monomers it might contain. The chosen treatment is maintained until all the gel has been transformed into an easily malleable paste, also storable at low temperatures.

As already stated, stage c) consists in leaving the paste to settle at ambient temperature in order that the remainder of free monomers that it might have retained, may be lost by exudation.

Stage d) consists in the preparation of the transparent varnish or lacquer and it implies dissolving the paste obtained in stage c) in established ponderal relations (according to the desired fluidity), with the mixture of monomers reticulants and binder without prepolymerization formulated in stage a). The transparent varnish is generally prepared with 60 parts in weight of the settled paste, and 40 ponderal parts of said monomers mixture. This operation is carried out at a temperature not exceeding ambient temperature, for instance with a cutting blades mixer, checking the temperature and cooling if necessary. It is desirable to leave the solution to settle one or two days so that it may age and clarify, proceeding then to screen or sieve filtering. This product, storable at low temperatures ( $-15^{\circ}$  /  $-20^{\circ}$  C) is a transparent lacquer or varnish ready to be immediately used or left to age as indicated above.

The final stage e) refers to the preparation of the pigmented ink or lacquer, by mixing the transparent varnish with the pigment or mixture of micronized pigments.

The quantity of pigment obviously depends on the covering power of the chosen pigment and the intensity of the color desired. The mixture is then processed very conveniently in a ball mill or tumbling device. Lacquers storable at  $-15^{\circ}$  /  $20^{\circ}$  C during periods of up to six months, with no noticeable changes, are obtained.

It is thus possible to obtain "type" or "mother" pigmented lacquers of each color, of which, according to requirements, fractions of invariable composition and characteristics may be extracted, ensuring in this manner the obtention of colors with constant shade and intensity.

Although the pigmented or colorless lacquers or varnishes obtained with the method herein described, may be used in all the conventional color application or coating techniques: brush, offset printing, aspersion, etc., the preferred method is the offset tampographic printing (offset pad printing) as mentioned in Argentine Patent Applications 301.045, 308.046 and 311.845. This also implies that the printing may be made over the surface of the finished lens or at any prior stage in its production, in conventional "sandwich" or on any stratum of the lens body, or intermediary dies, according to its design and features.

Prior to applying the pigmented varnish on the transparent contact lens, it is activated by adding an appropriated polymerization catalyzer (for thermal polymerization) such as USP 245 or Lupersol 256 (vide supra). It is desirable to detonize the transparent lenses (to eliminate the static electricity) prior to coloring. Once the coloring process is completed, the compound is baked at  $100^{\circ}$  /  $110^{\circ}$  C during 10/12 hours, and in the case of hydrophilic lenses, they are hydrated according to the conventional practice or as most convenient to the constituent material.

As a reference, examples of the preparation of polymerizable formulations for stage a) of the method under the present invention are included:

Example 1	
- N-vinyl-2-pyrrolidone	73.9 %
- 2-Hydroxyethyl methacrylate	12 %
- Monomethyl methacrylate	13 %
- Methacrylic Acid	0.50%
- Allyl methacrylate	0.30%
- Diallyl maleate	0.30%

9% of glycidyl acrylate and 0.11% of Diproxid is added as a catalyzer to the total mixture.

**Example 2**

- N-vinyl-2-pyrrolidone	67.18%
- 2-Hydroxiethyl methacrylate	20 %
- Cyclohexyl methacrylate	11.81%
- Allyl methacrylate	0.45%
- Ethyleneglycol dimethacrylate	0.45%

11% of glycidyl acrylate and 0.16% of Diproxid is added as catalyzer to this mixture.

**Example 3**

- Monomethyl methacrylate	98.90%
- Methacrylic acid	0.50%
- Allyl methacrylate	0.30%
- Diallyl maleate	0.30%

14% of glycidyl acrylate and 0.20% of Diproxid as catalyzer is added to this mixture.  
The lacquer formulations to obtain the most common colors are as follows:

**Example 4****Blue color**

Lacquer	60.66%
White	14.70%
Blue	8.08%
Red	1.97% (in drops)
Monomer	16.50%

**Example 5****Violet color**

Lacquer	51.43%
Violet	2.86%
White	28.56%
Black	8.57%
Monomer	8.57%

**Example 6****Green color**

Lacquer	73.61%
Green	2.71%
Yellow	1.24%
Black	2.51%
White	9.70%
Monomer	10.23%

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Example 7	
Hazel color	
Lacquer	49.88%
Brown	4.16%
Yellow	11.40%
White	14.61%
Monomer	19.95%

15 The pigments used in the preparation of the colored lacquers are well known and their names are the following:

**Green Hostaperm 86**

20 Cu phthalocyanine  
CI 74265 Green Pigment

**Blue Hostaperm A2R**

25 Stable modification of the Cu phthalocyanine  
CI 74160 Blue pigment 15:1

30 **Violet Hostaperm Special**

Dioxazine pigment  
CI 51319 Violet pigment 13

35

**Yellow Hostaperm HAG**

Monoazoic pigment of the benzimidazolone range  
CI 13980

40

**Brown Hostaperm HFL (Hazelperm-Braun HFL)**

Benzimidazolone pigment  
45 CI 13980  
Brown Pigment 32  
Solid white (TCO<sub>2</sub> PV-R-01 Hoechst)

As it may be noticed, the outstanding advantages of the present invention are:

- durability of the lens and color layer binding;
- 50 - simplicity in the formulation and storage of the colored or colorless lacquer and its intermediary preparations;
- versatility of the colored or colorless lacquer, that may be applied regardless of the constituent chemical groups of the substratum to be colored or covered;
- remarkable reduction of production costs.

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**Claims**

1. A method for the preparation of pigmented lacquers or varnishes for coloring contact lenses, comprising the steps of:

- a) prepolymerizing under UV radiation of 375/420 wavelength, half of a mixture of:
  - 60 to 70 of N-vinyl-2-pyrrolidone;
  - 5 - 8 to 12% of hydroxyethyl methacrylate;
  - 0.3 to 1% of reticulant components;
  - up to 13% of cyclohexyl methacrylate or acrylate;
  - 8 to 15% of glycidyl acrylate or methacrylate, as binding agent;
  - up to 1% acrylic or methacrylic acid;
  - 10 - 0.1 to 0.5% of UV diisopropylxanthogendisulfite, as photoinitiator of polymerization;
 the above values representing parts in weight for each 100 ponderal parts, under stirring and at ambient temperature, during a period of time sufficient to form a mass of oily consistency, which when radiation is turned off and is rapidly cooled in a  $-30^{\circ}/-40^{\circ}$  C bath, changes into a gel storable at low temperatures ( $-10^{\circ}/25^{\circ}$  C);
- 15 b) extracting the free monomers from said gel until an easily malleable paste is formed;
- c) letting the paste settle at ambient temperature, so that it may lose by exudation the remainder of free monomers it might contain;
- d) dissolving this paste with part of the mixture of liquid monomers without prepolymerization indicated in point a), in ponderal relation sufficient to form a solution at a temperature not higher than
 20 ambient temperature, then filtering and recovering a transparent, colorless and curable lacquer, to be kept between  $-18^{\circ}/-25^{\circ}$  C.
- e) pigmenting the lacquer of point d), mixing it with the necessary quantity of the chosen micronized pigments.

25 2. The method according to claim 1, wherein the components N-vinyl-2-pyrrolidone and 2-hydroxyethyl methacrylate of point a) in claim 1, are replaced with similar values of monomethyl methacrylate.

3. The method according to claims 1 and 2, wherein the prepolymerization of the monomers mixture is carried out by heat, replacing the UV photoinitiators with benzoyl peroxide, Lupersol 256, USP 245; or azobisisobutyronitrile in similar proportions.

30 4. The method according to claims 1, 2 and 3 wherein the reticulation component is chosen among diallyl maleate, ethyleneglycol acrylate or methacrylate, trimethyl propanol dimethacrylate and tri or tetraethylene dimethacrylate and mixtures thereof.

5. The method according to claims 1, 2, 3 and 4 wherein ethyleneglycol dimethacrylate and diallyl methacrylate, each one in a concentration of 0.15 to 0.50 in weight, are simultaneously applied as reticulant agents.

35 6. The method according to claims 1,2,4 and 5 wherein the UV photoinitiator is chosen among benzoyl and Darocur in ponderal concentration of 0.1 to 0.5%.

7. The method according to claim 1, wherein the monomers mixture comprises:  
60-80 of N-vinyl-2-pyrrolidone, 4 to 10% of 2-hydroxyethyl methacrylate, 0.30% of ethyleneglycol dimethacrylate, 0.30% of diallyl maleate and 12% of glycidyl acrylate, in relation to the total of the  
40 preceding components.

8. The pigmented lacquers or varnishes, applicable to coloring polymeric substrates, obtained with the methods of the above claims 1, 2, 3, 4, 5, 6 and 7.

9. The colorless lacquers or varnishes obtained with the method described in points a) to d) of claim 1, and those corresponding to above claims 2, 3, 4, 5, 6 and 7 for application as a layer over any compatible  
45 surface that warrants the solidarity of the binding between layer and substratum.

10. The hydrophilic, flexible and gas permeable colored contact lenses obtained applying by any method the pigmented lacquers or varnishes of above claims 1, 2, 3, 4, 5, 6 and 7 (prior activation of the same with USP 245 or Lupersol 256), either over finished transparent lenses or in previous production stages on any stratum of their bodies or intermediary dies, according to their designs and characteristics,  
50 with final curing by oven to  $100/110^{\circ}$  C during 10/12 hours, and posterior hydration, when they were hydrophilic lenses.







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**16.08.90 Bulletin 90/33**

(94) Designated Contracting States:  
**BE CH DE ES FR GB IT LI NL**

(96) Date of deferred publication of the search report:  
**10.04.91 Bulletin 91/15**

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**EP 0 382 005 A3**



European Patent  
Office

# EUROPEAN SEARCH REPORT

Application Number

DOCUMENTS CONSIDERED TO BE RELEVANT			EP 90101440.7
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. CL.5)
A	<u>US - A - 4 048 034</u> (MARTAN) * Claims; column 2, line 57 - column 3, line 2 * --	1,8-10	C 08 J 7/04 C 09 D 139/06 G 02 B 1/10
A	<u>GB - A - 1 441 108</u> (CYRIL AUBREY REDFARN) * Claims; page 4, lines 66-73 * -----	1,8-10	
			TECHNICAL FIELDS SEARCHED (Int. CL.5)
			C 08 J C 09 D G 02 B
The present search report has been drawn up for all claims			
Place of search <b>VIENNA</b>		Date of completion of the search <b>12-02-1991</b>	Examiner <b>PAMMINGER</b>
<b>CATEGORY OF CITED DOCUMENTS</b>			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- A : member of the same patent family, corresponding document	

• PPO FORM 150 (03/87 (1/90))